Superfluorescence from Chemically Pumped Iodine Molecules

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Stimulated emission from chemically formed excited iodine molecules has been observed. The emission originates from the vibrational state $v' = 55$ of $I_2(B^3\Pi)$. The excited molecules are produced by a three body recombination reaction.

In 1938 Porret and Goodeve [1] suggested that dissociation of methyl iodide by ultraviolet light results in formation of iodine atoms mostly in an excited state. The resulting population inversion of atomic iodine states was subsequently successfully utilized by Kasper and Pimentel [2] to produce stimulated 1315 nm infrared emission. Later studies [3, 4] showed that particularly high inversion occurs in the dissociation of perfluorinated alkyl iodides. Another important factor contributes to the high laser amplification in these systems: the excited iodine atoms in the $^2P_{1/2}$ state exhibit a very low deactivation rate in collisions with the parent molecules. Measurements of the effective lifetime of excited iodine atoms in the presence of perfluorinated alkyl iodides [5, 6] showed this to be almost equal to the natural lifetime under the experimental conditions.

In 1979 Stephan and Comes [7] discussed a chemiluminescence occurring during the photolysis of n-C_3F_7I; the effect was attributed to the recombination of two iodine atoms, one of them in the excited $^2P_{1/2}$ state:

$$I^*(^2P_{1/2}) + I(^2P_{3/2}) \rightarrow I_2^*(B\,^3\Pi),$$
$$I_2^*(B\,^3\Pi) \rightarrow I_2(X\,^1\Sigma) + h\nu. \qquad (1)$$

In this process excited iodine molecules in the B state are formed, as can be demonstrated by the observation of the well-known (B-X) emission. Kinetic analysis of the time dependence of the emitted radiation indicated for the photolysis of n-C_3F_7I a very high degree of inversion, nearly 100% when the fourth harmonic (266 nm) of the light of a Nd-YAG laser was employed.

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Analysis of the emitted spectrum with a resolution $\Delta\lambda/\lambda = 120$ showed a continuum beginning at the short-wavelength limit of the (B-X) emission (498.9 nm) and extending over a spectral range that agrees quite well with the laser-induced fluorescence (LIF) of I_2 produced by the 514.5 nm Ar^+ laser line. As further refinements enabled the spectral resolution to be increased by more than two orders of magnitude, to $\Delta\lambda/\lambda = 5 \times 10^4$, this chemiluminescence resulting from a three-body collision continued to appear as an unresolved continuum. Today we know from other studies that this quasi-continuous emission is brought about by the strong relaxation of the vibrationally and rotationally excited iodine molecules formed in the reaction, which results in a very broad occupancy of rotational and vibrational levels in the B state. These measurements have further shown that the electronically excited iodine molecules thus formed can, under certain experimental conditions, be made to undergo stimulated emission. Thus this process constitutes a chemically pumped molecular-iodine laser system.

The experimental setup in these studies was one designed to permit observation of the chemiluminescence under particularly pure and well-defined conditions. The rate of deactivation of iodine atoms in the $^2P_{1/2}$ state by collision with n-C_3F_7I is exceptionally low. The rate constant for the process

$$I^*(^2P_{1/2}) + n\text{-}C_3F_7I \rightarrow I(^2P_{3/2}) + n\text{-}C_3F_7I \qquad (2)$$

is $k_2 = 4.6 \times 10^{-17}$ cm^3 molec^{-1} s^{-1}, as determined by Stephan and Comes [7]. If, however, these excited iodine atoms collide with I_2, they are very efficiently deactivated; the probability of deactivation is 6×10^5 times as great as when the collision partner is n-C_3F_7I [8]. Thus, in order to minimize

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the photochemical production of I_2, the energy supplied for the primary photodissociation of n-C_3F_7I should be limited as much as possible. The luminescence spectrum was observed by means of a scanning monochromator, as described by Stephan and Comes [7]. The need for high purity precluded the use of a flow system; constant renewal of the reactant was required.

To satisfy this requirement for great purity, the measuring technique was altered, and the detection sensitivity greatly enhanced by two expedients: the use of imaging optics to improve the utilization of the isotropic fluorescence radiation, and use of a cooled optical multichannel analyzer as detector, permitting — in conjunction with a polychromator — instantaneous recording of the entire spectrum after each photolysis flash. Data acquisition and processing was performed by a microprocessor. The ability to record all needed spectra with one fixed setting of the polychromator also meant that wavelengths could be determined with great accuracy. The wavelength scale was calibrated by means of the LIF spectrum of I_2, excited by the 514 nm line of a single-mode Ar^+ laser. The experiments were performed under two different sets of conditions:

1. pure n-C_3F_7I at 6 Torr, and
2. n-C_3F_7I (6 Torr) mixed with argon (100 Torr).

The high sensitivity of the fluorescence detection system permitted acquisition of a chemiluminescence spectrum with as few as 5—10 photolysis flashes. Compared with the traditional method of observation, using a scanning monochromator, this represents a reduction by a factor of more than 1000 in the time required for one measurement.

Figure 1 shows that the "continuous" chemiluminescence spectrum (curve A), obtained with pure n-C_3F_7I, on addition of 100 Torr argon develops a pronounced band structure, (curve B), which can clearly be identified with the structure of the B-X emission. As the band emission grows in intensity, the "continuous" emission decreases correspondingly. A very similar result (curve C) is obtained by focusing the laser beam instead of adding argon. The diameter of the beam is reduced to about one-third of its original 3 mm value.

This last observation shows especially clearly the threshold nature of the emission phenomenon. Evidently the function of argon is only to maintain the necessary concentrations of I and I^*, and thus also that of I_2^*, which decreases by diffusion in the system. Alternatively, the loss by diffusion can be offset by substantially increasing the initial concentration of iodine atoms, in the volume in which they are produced, by focusing the photolysis beam.

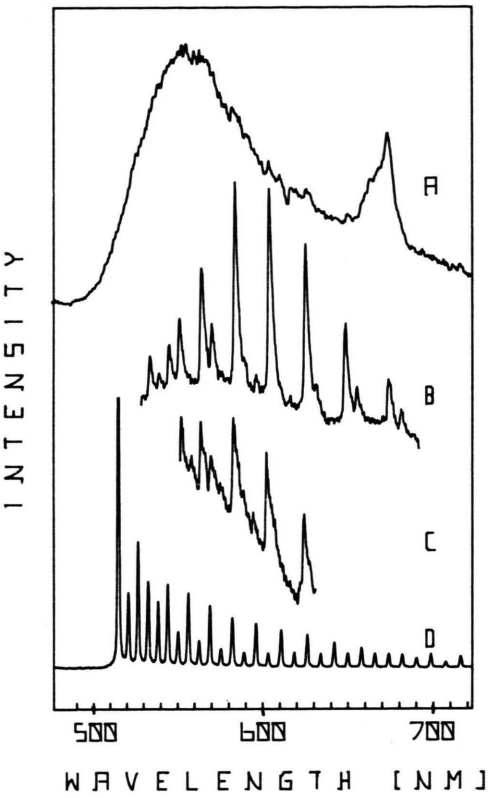

Fig. 1. I_2 (B-X) emission and superfluorescence, uncorrected for spectral response of the Optical Spectrum Analyser with the following experimental conditions. A) pure n-C_3F_7I at 6 torr, B) n-C_3F_7I at 6 torr plus argon at 100 torr, C) pure n-C_3F_7I at 6 torr with focussed photolysis beam, D) pure I_2 at 0.033 torr excited with the 514.5 nm Ar^+-laserline to B $^3\Pi$, $v'=43$, $J'=12$, 16. As A) and D) were recorded using a 600 lines/mm grating, while a 1200 lines/mm grating was used for B) and C), the spectral region covered in B) and C) only partially overlaps that in A) and D).

The spectra shown in Fig. 1, curves B and C, can be unambiguously identified with the B-X emission of the iodine molecule. As is easily seen that I_2 fluorescence bands are red shaded. The superfluorescence lines have a common upper laser level of either $v'=48$ or $v'=55$. The corresponding lower laser levels are either the vibrational levels $v''=9$, 12, 15, 18, 21, and 24 or the vibrational levels $v''=10$, 13, 16, 19, 22, and 25 in the electronic ground state. The assignment to the 48 progression or the

55 progression follows from the position of the five most intense superfluorescence lines relative to the lines of the LIF of I_2 excited by the 514 nm Ar^+ laser line. Since the initial vibrational level is the same for all the principal lines, their spacing is determined by the spacing of the ground state vibrational levels, that is, $\Delta v'' = 3$. A spectroscopic assignment of super-fluorescence lines can also be performed by comparing the experimentally determined spacings of the five principal lines with the spacings calculated from established molecular data [9, 10] taking anharmonicity of the potential into account. To this end, the sum of squares of the deviations of experimentally determined energies from the calculated values is calculated as a function of the lower energy level. The smallest such sum is found for $v'' = 10$ as the lower laser level for the first of the five principal lines. This choice also identifies $v' = 55$ as the common upper level.

Since the optical multichannel analyzer has an S-20 R characteristic, the spectrum can be recorded only in the visible range. In view of the large Franck-Condon factors in the IR [11], superfluorescence is to be expected in that region, also. Thus the observed superfluorescence of the excited iodine molecule is mainly emitted from a single vibrational state of I_2 in the B state.

As expected, slight contamination of the system by photochemically produced I_2 kills the superfluorescence, while the normal chemiluminescence, although apparently weakened, continues to exist. This is further evidence for the threshold nature of the radiation under investigation.

Superfluorescence from I_2 in the B state has also been obtained by optical pumping [12, 13]. However, the radiative characteristics of optically-pumped I_2 lasers are very different from those of the present chemically-pumped system, as can be particularly clearly seen from the intensity relationships in the emission. In the system studied by us, transitions with $\Delta v'' = 3$ are distinctly preferred, while the optically-pumped I_2 laser exhibits a sequence for which $\Delta v'' = 2$ [14, 15, 16].

While, for the optically-pumped I_2 laser, the 514 nm Ar^+ laser line excites only two rotational levels of the $v' = 43$ vibrational level, a more extensive distribution over rotational states is to be expected in the case of the chemically-pumped laser.

Preparations are being made to investigate the mechanism of formation of the upper laser state by use of an optical resonator, in the hope of elucidating the role of rotational excitation in the laser process.

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